

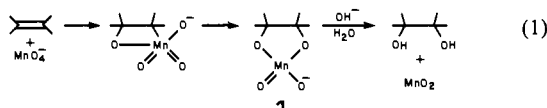
# Oxidation of Hydrocarbons. 18. Mechanism of the Reaction between Permanganate and Carbon-Carbon Double Bonds

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**Abstract:** The nature of the products obtained when permanganate reacts with olefins is determined by rapid reactions that occur after the rate-limiting step (which is known to involve the formation of an intermediate cyclic manganate(V) diester). A study of the reactions of manganate(V) oxide has shown that its primary reactions are disproportionation and oxidation to manganate(VI) by permanganate. Disproportionation is slow under highly basic conditions ( $k_2 = 6.9 \text{ M}^{-1} \text{ s}^{-1}$  in 3 M KOH) and very rapid under moderately basic or neutral conditions ( $k_2 > 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at pH 12). The converse is true for the reaction between manganate(V) and permanganate ( $k_2 = 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  in 3 M KOH and  $72 \text{ M}^{-1} \text{ s}^{-1}$  at pH 12). Consequently, although the principle reaction of the intermediate cyclic manganate(V) diester is likely disproportionation under neutral conditions, oxidation is the primary reaction in very basic solutions. It is shown how these kinetic measurements account for the observed products—diols in basic solutions and ketols under neutral conditions.

The oxidation of organic compounds by permanganate ion has been extensively studied in several laboratories during the past century. The first investigations consisted primarily of an identification of the organic products that can be obtained under various conditions. Such studies occasionally yielded remarkable insights into the mechanism of the reaction. Most notably, the observation that treatment of alkenes with permanganate under alkaline conditions results in syn dihydroxylation led Wagner<sup>1</sup> to propose that the reaction proceeds by way of a cyclic manganate(V) diester, **1**, as indicated in eq 1.



In more recent times, extensive kinetic studies have shown that the reactions of permanganate with alkenes exhibit inverse secondary isotope effects<sup>2</sup> as would be expected if the reaction involved a transition state in which the hybridization of the olefinic carbon atoms had changed from  $sp^2$  to  $sp^3$ . It has also been found that the reaction of permanganate with a particular unsaturated compound proceeds at approximately the same rate under different conditions and that similar activation parameters (small  $\Delta H^\ddagger$  and large  $-\Delta S^\ddagger$ ) are always observed.<sup>2</sup> This similarity in rate constants and activation parameters is surprising because quite different products are obtained when conditions are changed. For example, as mentioned above, oxidation under alkaline conditions leads to *cis*-diols and manganese dioxide, while the same reaction under acidic conditions results in cleavage of the double bond to give carbonyl compounds along with  $\text{Mn}^{3+}$  or  $\text{Mn}^{2+}$ . Moreover, under neutral conditions a third organic product, the corresponding ketol, is obtained in moderate to high yields.<sup>3</sup>

These observations, taken together, have led to the conclusion that all permanganate/alkene reactions proceed via similar transition states but that the nature of the products is determined by a series of post-transition-state reactions, which are highly dependent upon conditions. Reactions such as the one depicted in eq 1, therefore, conceal more than they reveal. The observation that manganese in the cyclic diester, **1**, is in a +5 oxidation state, while the product is +4 or +6 under basic conditions and +3 or +2 under acidic conditions, leads to a series of questions concerning the nature of the reactions that must occur when the intermediate

is converted into products. Several authors have speculated on the nature of the reactions, but, as far as we have been able to determine, no experimental evidence directly bearing on these questions has been published.

In an attempt to improve our understanding of the nature of the product-forming steps in these reactions, we have undertaken to synthesize manganese species in all possible oxidation states between +7 and +4, determine the types of reactions they undergo, and estimate the rate constant for each possible reaction. The reaction of each manganese compound with itself (disproportionation), with the solvent, with each of the other manganese compounds, and with the organic substrates has also been studied. In this way it has been possible to identify those reactions that occur most readily under a particular set of conditions and to thereby achieve an understanding of the reaction sequences that follow the transition state.

Manganese species in the +5 and +6 oxidation states were synthesized using previously published procedures. A molecular manganese(IV) species was prepared by a procedure that involves the photochemical-induced reduction of permanganate.<sup>4</sup> Since some of these manganese compounds are stable only in fairly alkaline solutions, it was necessary to occasionally extrapolate to a common set of conditions before comparisons could be made.

## Experimental Section

**Preparation and Properties of Manganate(VI).** Solutions of manganate(VI) were prepared according to the procedure reported by Carrington and Symons.<sup>5</sup> In a typical procedure, potassium permanganate was added to a highly alkaline solution (5–10 M KOH) at room temperature and stirred for 24 h. The spectrum of the resulting solution was identical with that reported for solutions of  $\text{MnO}_4^{2-}$ .

**Preparation and Properties of Manganate(V).** Manganate(V) was prepared by adding a theoretical amount of hydrogen peroxide to an ice-cold solution of manganate(VI) in 10 M KOH. The resulting sky blue solution was stirred for about 4 h and then filtered to remove particles of  $\text{MnO}_2$ . The UV-vis spectrum of this solution was identical with that previously published for manganate(V).<sup>6</sup> Under these very basic conditions it is expected to exist primarily as  $\text{HMnO}_4^{2-}$  along with equilibrium amounts of  $\text{MnO}_4^{3-}$  and  $\text{H}_2\text{MnO}_4^-$ .

**Preparation and Properties of Manganate(IV).** A stable aqueous solution of manganate(IV) was prepared by photolysis of dilute solutions of potassium permanganate.<sup>4</sup> In a typical procedure, a neutral, dilute solution of  $\text{KMnO}_4$  was photolyzed using a medium-pressure Hanovia mercury lamp surrounded by a double-walled Pyrex tube through which cold water could be circulated to minimize heat transfer from the lamp

(1) Wagner, G. *J. Russ. Phys.-Chem. Soc.* **1895**, 27, 219.

(2) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1974**, 96, 5517. Lee, D. G.; Brown, K. C. *J. Am. Chem. Soc.* **1982**, 104, 5076.

(3) Stewart, R. *Oxidation Mechanisms*; Benjamin: New York, 1964; Chapter 5. Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, IL, 1981.

(4) Lee, D. G.; Moylan, C. R.; Hayashi, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, 109, 3003.

(5) Carrington, A.; Symons, M. C. R. *J. Chem. Soc.* **1956**, 3373.

(6) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A, p 14.

**Table I.** Reaction Order for the Disproportionation of Manganate(VI)

pH	order <sup>a</sup>	correlation coeff	pH	order <sup>a</sup>	correlation coeff
9	1.94 ± 0.04	0.9995	11	2.04 ± 0.08	0.9978
10	1.99 ± 0.02	0.9998			

<sup>a</sup>Order with respect to  $[\text{MnO}_4^{2-}]$  obtained from plots of  $\log(\text{initial rate})$  vs  $\log A$ . Each result is the average of at least three experiments. Temperature 25.0 °C.

to the solutions. As the reactions proceeded, aliquots were withdrawn and analyzed with the aid of a UV-vis spectrophotometer. A compound with intense absorbance bands at 368 nm ( $\log \epsilon = 4.03$ ) and 219 nm ( $\log \epsilon = 3.90$ ) formed as the concentration of permanganate decreased. Iodometric titrations indicated that the manganese in this species was in the +4 oxidation state.

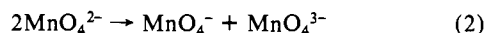
These solutions are stable between pH 3 and 12. When the pH becomes greater than 12, precipitation occurs, while below pH 3 the solution slowly bleaches. Under neutral conditions the manganate(IV) solutions could be concentrated from 0.0005 to 0.02 M and diluted back to 0.0005 M without loss of spectral integrity. However, attempts to increase the concentration to 0.05 M resulted in the formation of precipitated  $\text{MnO}_2$ . When the 0.0005 M solution was heated at 90 °C for 4 h, no change in the spectrum could be detected, and no precipitation occurred.

**Kinetic Methods.** The rates of the reaction were determined spectrophotometrically. The slower reactions were monitored using an HP-8450A UV-vis spectrophotometer, and the faster reactions were followed using an Update System 777 rapid-scanning stopped-flow spectrophotometer modified somewhat to accommodate our studies.

## Results

**Reactions of Manganate(VI).** Although manganate(VI) is stable under highly basic conditions, disproportionation occurs when the pH is decreased. Since the reaction is very rapid, the rates were followed using a stopped-flow spectrophotometer. A stock solution of manganate(VI) in 1.25 M KOH was placed in one syringe and a concentrated buffer solution (pH = 9.00) in the other syringe. The instrument was adjusted so that 0.20 mL of the manganate(VI) solution and 1.00 mL of the buffer solution were simultaneously forced through the mixing chamber and into the observation cell. Spectra of the resulting solutions were then collected at intervals of 80–100 ms.

One of the products,  $\text{MnO}_4^{3-}$ , which forms during the disproportionation of manganate(VI) (eq 2), is also unstable and, as



will be described in the next section, also disproportionates with the formation of  $\text{MnO}_2$ , an insoluble product. Because of these consecutive reactions, an isosbestic point is not observed, and the rate law was consequently determined using initial reaction rates. As has been described elsewhere,<sup>7</sup> the initial reaction rate can easily be obtained by fitting a plot of absorbance (at 610 nm in this case) vs time to eq 3 where  $A$  is the absorbance at time  $t$ , and  $a_i$  are constants. The initial rates can then be determined by taking the first derivative (eq 4) and setting time equal to zero (eq 5).

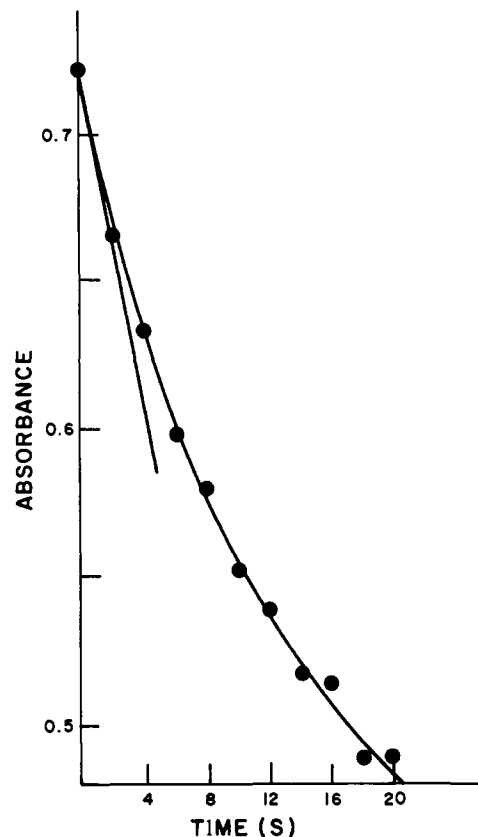
$$A = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 \quad (3)$$

$$dA/dt = a_1 + 2a_2 t + 3a_3 t^2 \dots \quad (4)$$

$$dA/dt = a_1 \quad (t = 0) \quad (5)$$

Typical data for this reaction have been plotted in Figure 1.

The order of the reaction, obtained from plot of  $\log(-dA/dt)$  vs  $\log A$  was found to be 2 for pH = 9–11 (Table I). The rate of reaction was also found to be inversely dependent on the pH of the solution (Table II). A reaction scheme consistent with these observations is given in eq 6–8. The fate of the manganate(V) species,  $\text{H}_2\text{MnO}_4^-$ , formed in this sequence is discussed in the next section.



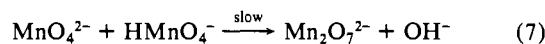
**Figure 1.** Typical rate plot for the disproportionation of  $\text{MnO}_4^{2-}$  at pH 9. The circles are experimental data, the curve is the theoretical fit, and the straight line is the tangent to the curve at time = 0.

**Table II.** Rate Constants for the Disproportionation of Manganate(VI)

pH	$[\text{MnO}_4^{2-}]$ , $\text{M} \times 10^4$	$k_2$ , <sup>a</sup> $\text{M}^{-1} \text{s}^{-1}$
9	2.93	173.8 ± 7.3
9	4.30	190.9 ± 5.3
9	5.70	164.2 ± 2.0
9	6.09	166.0 ± 1.5
9	7.04	169.1 ± 1.5
10	3.06	34.3 ± 1.8
10	4.10	34.0 ± 1.2
10	5.10	35.0 ± 2.7
10	6.16	33.8 ± 1.2
10	6.48	33.9 ± 1.3
10	7.65	33.9 ± 0.8
11	3.06	5.6 ± 0.1
11	4.01	4.9 ± 0.1
11	6.45	5.5 ± 0.1
11	7.46	5.7 ± 0.1
11	8.37	5.3 ± 0.1

<sup>a</sup>Each datum is the average of three experiments at  $25.0 \pm 0.1$  °C.

nate(V) species,  $\text{H}_2\text{MnO}_4^-$ , formed in this sequence is discussed in the next section.



In order to avoid solubility problems in water, the kinetics of the reactions between manganate(VI) and carbon-carbon double bonds was studied using two unsaturated carboxylic acids (cinnamic and crotonic) as substrates. Disproportionation of  $\text{MnO}_4^{2-}$  was minimized by retaining it in a highly basic solution until the reaction was initiated through addition of substrate in a solution

(7) Chandler, W. D.; Lee, E. J.; Lee, D. G. *J. Chem. Educ.* **1987**, *64*, 878.

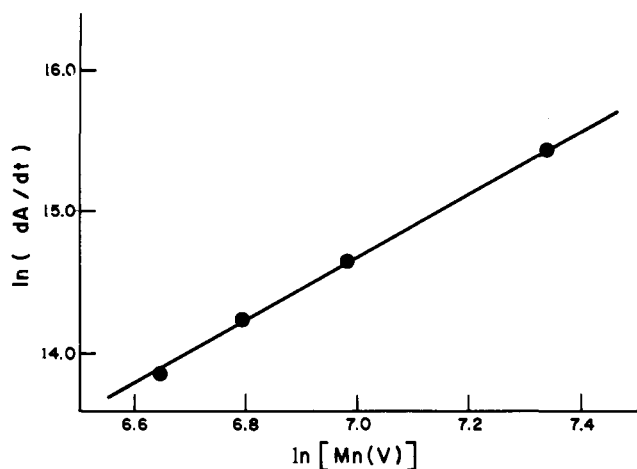


Figure 2. Plot of  $\ln(dA/dt)$  vs  $\ln[Mn(V)]$  for the disproportionation of manganate(V) in 6.0 M KOH. Slope = 2.07.

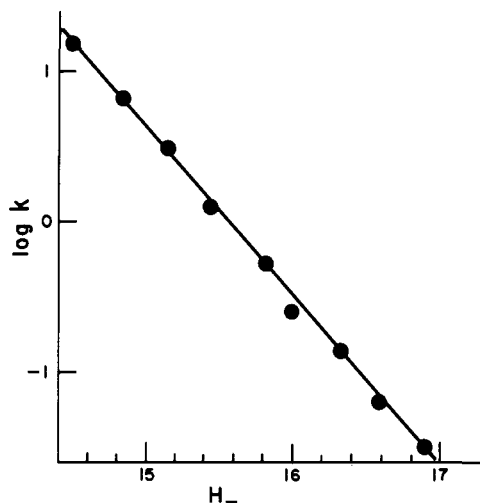


Figure 3. Plot of  $\log k$  vs  $H_-$  for the disproportionation of manganate(V).

of lower base concentration. In a typical experiment, an aliquot (1.0 mL) of  $MnO_4^{2-}$  in 3.0 M KOH was transferred to a 1.0-cm cuvette, 1.0 mL of substrate added, the resulting solution quickly mixed, and the cuvette placed in the thermostated cell compartment of a Hewlett Packard 8450A spectrophotometer. The reaction rate was monitored by following the decrease in absorbance at 610 nm. Because manganese dioxide precipitated as the reaction progressed, it was impossible to follow it to completion, and the initial rate method described above was used to determine the rate law and constants.

The order with respect to  $MnO_4^{2-}$ , obtained from plots of  $\ln(-dA/dt)$  vs  $\ln A_0$  at constant substrate concentration, was found to be unity, as was the order with respect to substrate. The second-order rate constants are independent of base concentration as illustrated by the data in Table III.

**Reactions of Manganate(V).** Disproportionation of manganate(V) results in the formation of a clear green solution (after centrifuging) with a spectrum similar to that of manganate(VI) and a precipitate of  $MnO_2$ . When the rate of reaction was monitored by following the increase in absorbance at 438 nm, a plot of  $\ln(dA/dt)$  vs  $\ln[Mn(V)]$  was linear with a slope of 2.0 (Figure 2). Hence, the reaction is second order with respect to the concentration of manganate(V). Although the rate of reaction increases as base concentration decreases, the order remains constant (Table IV). The logarithms of the rate constants are, in fact, inversely proportional to the basicity function,  $H_-$  (Figure 3).

The reaction between manganate(V) and permanganate results in the formation of manganate(VI), as in eq 9.

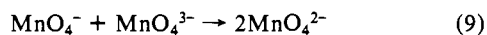


Table III. Rate Constants for the Reaction between Manganate(VI) and Crotonate Ion in Different Concentrations of Base<sup>a</sup>

[KOH], M	[crotonate], M × 10 <sup>3</sup>	[MnO <sub>4</sub> <sup>2-</sup> ], M × 10 <sup>4</sup>	slope, <sup>b</sup> M s <sup>-1</sup> × 10 <sup>7</sup>	k <sub>2</sub> , <sup>c</sup> M <sup>-1</sup> s <sup>-1</sup> × 10
10.0	3.00	8.18	4.11 ± 0.30	1.67 ± 0.12
10.0	5.00	8.14	6.72 ± 0.52	1.65 ± 0.13
10.0	7.00	8.16	9.41 ± 0.30	1.65 ± 0.05
10.0	11.00	8.09	13.75 ± 0.31	1.55 ± 0.03
10.0	13.00	8.02	16.73 ± 0.45	1.60 ± 0.04
7.5	3.00	7.56	4.32 ± 0.24	1.90 ± 0.11
7.5	5.00	7.53	5.54 ± 0.60	1.47 ± 0.15
7.5	6.00	7.40	7.15 ± 0.13	1.38 ± 0.03
7.5	9.00	7.54	10.35 ± 0.79	1.53 ± 0.12
7.5	11.00	7.55	14.93 ± 0.90	1.80 ± 0.11
7.5	13.00	7.56	16.43 ± 0.45	1.66 ± 0.05
7.5	13.00	4.93	8.68 ± 0.49	1.35 ± 0.08
7.5	13.00	3.02	5.87 ± 0.36	1.50 ± 0.09
7.5	13.00	1.91	4.08 ± 0.25	1.64 ± 0.10
5.0	3.00	7.29	3.96 ± 0.24	1.81 ± 0.11
5.0	5.00	7.17	6.75 ± 0.60	1.88 ± 0.17
5.0	9.00	7.31	9.92 ± 0.13	1.51 ± 0.02
5.0	11.00	7.30	14.40 ± 0.79	1.79 ± 0.10
5.0	13.00	7.21	13.99 ± 0.45	1.49 ± 0.05
5.0	13.00	5.17	8.75 ± 0.51	1.30 ± 0.08
5.0	13.00	3.90	7.50 ± 0.40	1.48 ± 0.08
5.0	13.00	2.61	5.38 ± 0.36	1.59 ± 0.11
5.0	13.00	2.08	4.78 ± 0.24	1.77 ± 0.09
3.0	3.00	6.81	3.17 ± 0.31	1.55 ± 0.15
3.0	5.00	6.65	4.76 ± 0.61	1.43 ± 0.18
3.0	7.00	6.73	8.02 ± 0.48	1.70 ± 0.10
3.0	9.00	6.74	9.08 ± 0.87	1.50 ± 0.14
3.0	13.00	6.96	14.10 ± 0.78	1.56 ± 0.09
3.0	13.00	4.95	11.53 ± 0.57	1.79 ± 0.09
3.0	13.00	3.77	8.93 ± 0.15	1.82 ± 0.03
3.0	13.00	2.68	5.82 ± 0.19	1.67 ± 0.05
1.5	3.00	3.57	1.91 ± 0.15	1.78 ± 0.14
1.5	5.00	3.58	2.87 ± 0.28	1.60 ± 0.16
1.5	7.00	3.56	4.66 ± 0.37	1.87 ± 0.15
1.5	9.00	3.58	5.91 ± 0.34	1.83 ± 0.11
1.5	13.00	6.96	13.53 ± 0.55	1.50 ± 0.06
1.5	13.00	5.44	10.87 ± 0.45	1.54 ± 0.06
1.5	13.00	4.21	8.74 ± 0.61	1.60 ± 0.11
1.5	13.00	2.83	6.53 ± 0.52	1.77 ± 0.14

<sup>a</sup> Temperature 25.0 ± 0.1 °C. Each datum is the average of at least three experiments. <sup>b</sup> Initial slope obtained as described in the text. <sup>c</sup> k<sub>2</sub> = slope/[MnO<sub>4</sub><sup>2-</sup>][crotonate].

Table IV. Rate Constants for the Disproportionation of Manganate(IV)

[KOH], M	order	k <sub>2</sub> , <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup>	[KOH], M	order	k <sub>2</sub> , <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup>
3.0	2.02	7.10	7.0	2.03	0.13
3.0	2.00	6.69	7.0	2.07	0.26
3.0	2.04	7.10	7.0	1.95	0.25
4.0	2.00	3.00	8.0	2.00	0.13
4.0	2.00	2.89	8.0	2.00	0.14
4.0	2.00	3.00	8.0	2.00	0.14
5.0	2.00	1.22	9.0	2.03	0.064
5.0	2.00	1.25	9.0	2.07	0.065
5.0	2.03	1.25	9.0	2.00	0.063
6.0	1.96	0.53	10.0	2.13	0.034
6.0	2.03	0.54	10.0	2.00	0.034
6.0	2.00	0.54	10.0	2.00	0.031

<sup>a</sup> Order with respect to [Mn(V)]. <sup>b</sup> An induction period was observed for high base concentrations (6.0–10.0 M KOH).

In a typical experiment, 0.2 mL of manganate(V) in 5.0 M KOH was reacted with 1 mL of permanganate in 0.10 M KOH using the stopped-flow apparatus described above. The reaction (in 0.92 M KOH) then proceeded with a decrease in the absorbance peaks due to permanganate and an increase in a broad peak at 610 nm to give a final spectrum that had all the features of manganate(VI).

Good second-order kinetic plots were obtained (Figure 4), and the rate of reaction was found to be directly dependent on base concentration (Figure 5).

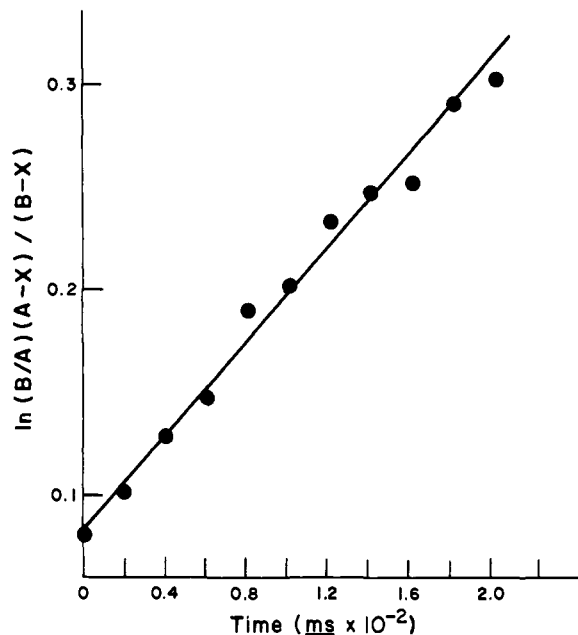


Figure 4. Second-order plot for the oxidation of manganate(V) ( $1.2 \times 10^{-4}$  M) by permanganate ( $2.2 \times 10^{-4}$  M) in 1.08 M KOH at 3.0 °C. Slope =  $1.12 \pm 0.05$  s $^{-1}$ .  $r = 0.992$ .

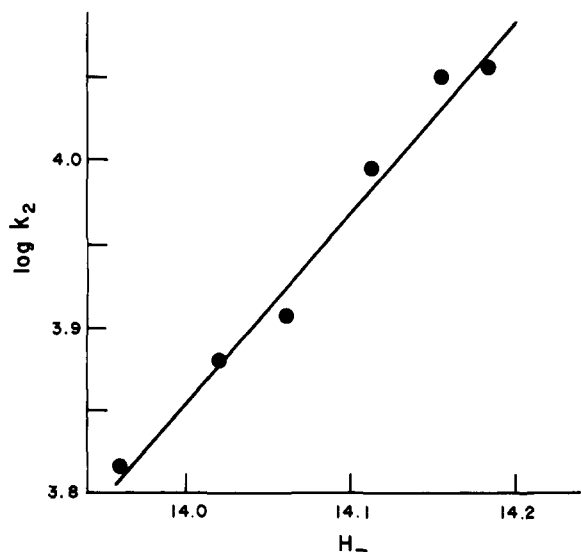
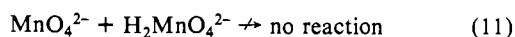
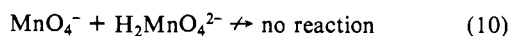


Figure 5. Plot of  $\log k_2$  vs  $H_-$  for the oxidation of manganate(V) by permanganate at 3.0 °C. Slope =  $1.17 \pm 0.08$ .  $r = 0.990$ .

The essential result emerging from these studies is that the disproportionation of manganate(V) is slow at high base concentrations but very fast at low basicities while the converse is true for its reaction with permanganate (Figure 6). Surprisingly, it was found that manganate(V) did not react with either crotonate or cinnamate at measurable rates.

**Reactions of Manganate(IV).** Manganate(IV) was found to react with unsaturated organic compounds, but only under acidic conditions. In the alkaline solutions used in this study, manganate(IV) was not reduced by compounds containing carbon-carbon double bonds. Similarly, manganate(IV) failed to react with either permanganate or manganate(VI) (eq 10 and 11).



In summary, manganate(IV) appears to be stable and unreactive under basic conditions.

**Reactions of Permanganate.** In addition to the reactions of permanganate with manganate(V) and -(IV), as described above,

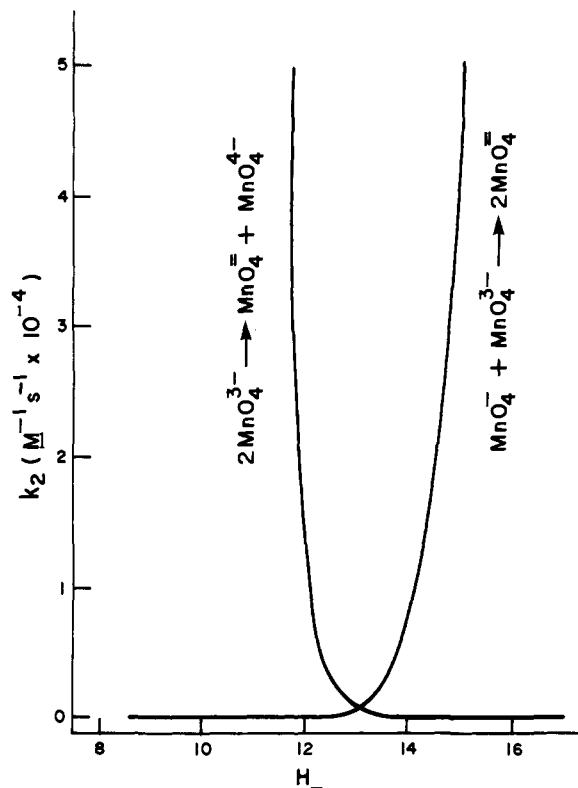


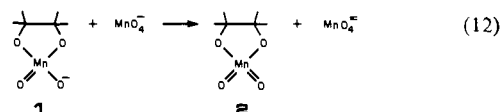
Figure 6. Calculated second-order rate constants for the disproportionation of manganate(V) and the oxidation of manganate(V) by permanganate.

a study was made of its reactions with crotonate under basic conditions.

The order of the reaction was found to be unity with respect to both oxidant and reductant, and base dependence was characterized by a broad region (below pH 14) where the rate was almost constant and a region of higher basicity where the rate was directly proportional to the basicity constant,  $H_-$ .

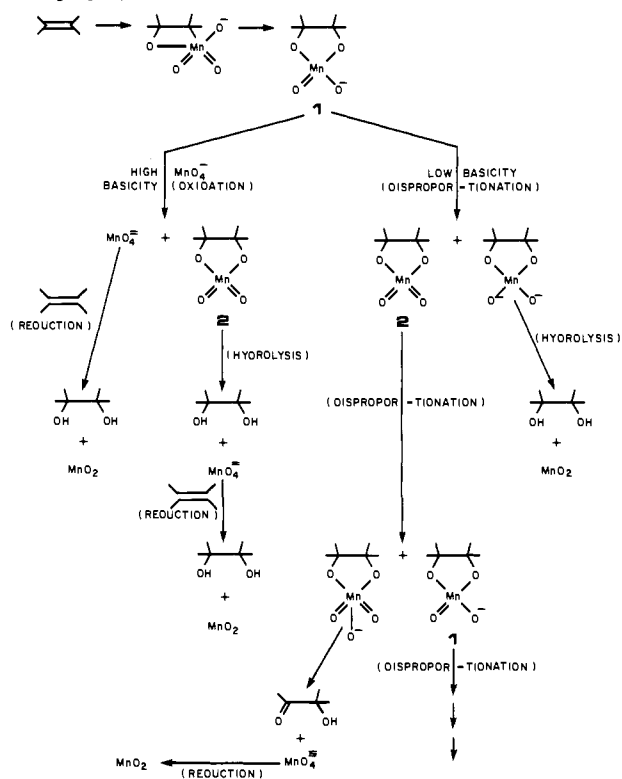
#### Discussion

All experimental and theoretical evidence available is consistent with the suggestion first made nearly a century ago that permanganate reacts with carbon-carbon double bonds to form a cyclic manganate(V) diester as in eq 1. Under basic conditions, where the final product of the reaction is manganate(VI), the initial reaction must be followed by a subsequent step in which the cyclic diester is oxidized by permanganate as in eq 12.



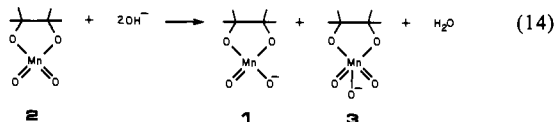
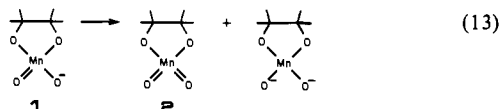
This suggestion, which is consistent with the observation that manganate(V) reacts rapidly with permanganate under basic conditions (Figure 6), can be verified by measuring the rate at which the produced manganate(VI) reacts with excess crotonate. If all of the manganate(VI) exists as the free ion,  $\text{MnO}_4^{2-}$ , the rate of the reaction with excess substrate should be identical with that observed when manganate(VI) and substrate solutions are mixed as previously described. On the other hand, if half of the manganate(VI) exists as a cyclic diester (as suggested by eq 12), the observed rate would be expected to be greater or less than predicted, depending on whether the cyclic diester is more or less reactive than  $\text{MnO}_4^{2-}$ . In fact, it was found experimentally that the rate constant is almost exactly half of the predicted value when crotonate is used as the substrate. Consequently, it appears that the cyclic manganate(VI) diester formed in eq 12 does not react at an appreciable rate with excess crotonate, and it is therefore possible to conclude that reaction 12 follows reaction 1 when permanganate reacts with a stoichiometric amount of unsaturated

Scheme I. The Reaction of Permanganate with Carbon-Carbon Double Bonds

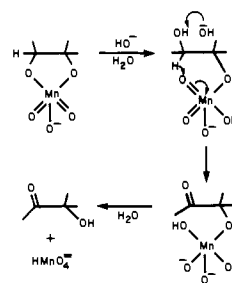


substrate under basic conditions. Of course, in the presence of excess substrate,  $\text{MnO}_4^{2-}$  will eventually be reduced to  $\text{MnO}_2$ .

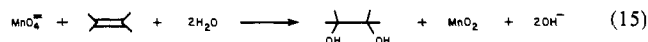
Under neutral or slightly basic conditions, the rate of reaction between manganate(V) and permanganate is decreased while the rate of disproportionation of manganate(V) increases (Figure 6). Hence, at low base concentrations it is likely that reaction 1 would be followed by disproportionation (eq 13). Since manganate(VI) also rapidly disproportionates under these conditions, cyclic esters in the +7 and +5 states would likely be formed from **2** as in eq 14.



Although there is no experimental evidence that can be used as a guide for the reaction of a cyclic manganate(VII) diester, **3**, it is quite possible that it is this species that leads to the formation of more highly oxidized organic products such as ketols that are known to be formed under neutral conditions:



When excess substrate is present, an additional reaction (eq 15) would also contribute to the total reaction sequence. However,



since the rate of this reaction is nearly independent of base concentration (Table III) while the disproportionation of  $\text{MnO}_4^{2-}$  is inversely dependent on base concentration, reaction 15 would contribute only at high basicities.

### Conclusion

Although it is ordinarily very difficult to identify reactions that occur after a rate-limiting step, it has in this case been possible to measure the rates of the most likely product-forming steps. From a consideration of the rate constants reported herein it is possible to conclude that the reaction sequence depicted in Scheme I must pertain under conditions of "high" and "low" basicity.

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**Supplementary Material Available:** Eight figures depicting (i) successive spectra obtained during the photolysis of a dilute solution of  $\text{KMnO}_4$ , (ii) successive spectra obtained during the oxidation of manganate(V) by permanganate, (iii) successive spectra obtained during the reaction between manganate(VI) and crotonate ion, (iv) a plot of  $\log(dA/dt)$  vs  $\log A$  for the disproportionation of manganate(VI) at pH 9, (v) a plot of  $\log(-dA/dt)$  vs pH for the disproportionation of manganate(VI), (vi) a plot of  $\ln(-dA/dt)$  vs  $\ln A$  for the oxidation of cinnamate ion by manganate(VI) in 3.0 M KOH, (vii) a plot of  $\ln(-dA/dt)$  vs  $\ln[\text{cinnamate}]$  for the oxidation of cinnamate ion by manganate(VI) in 3.0 M KOH, and (viii) a plot of  $\log k_2$  vs  $H_-$  for the oxidation of crotonate ion by permanganate (2 pages). Ordering information is given on any current masthead page.